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(54) WATER-INSOLUBLE BACTERIOSTATS IN SOAP AND DETERGENT SOLUTIONS

(71) We, MALMSTROM CHEMICAL CORP., a corporation organised and existing under the laws of the State of New Jersey, United States of America, having a place of business at 1501 West Elizabeth Avenue, Linden, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to compositions for use as shampoos, skin cleaners, and for like purposes. The invention is especially directed to the production of compositions of this character having normally water-insoluble bacteriostatic agents incorporated therein.

In recent years, a number of efforts have been made to impart antibacterial and antifungal properties to shampoos and other skin cleansing products. As a result of those efforts, numerous varieties of antibacterial liquid cleansers, soaps and detergent bars, as well as of "anti-dandruff" shampoos have been proposed and sold.

These known products usually derive their claimed antibacterial properties from the incorporation therein of antibacterial agents which are poorly or only slightly water-insoluble. Some of the slightly water-soluble antibacterial agents employed in these products may be quite readily solubilized in significant concentrations in aqueous fatty acid soap or anionic synthetic detergent solutions, usually with the aid of heat. Illustrative of these latter antibacterial agents is 2,2'methylenebis (3,4,6 - trichlorophenol) commonly referred to as hexachlorophene, a commercial variety of which is sold under the trademark "G-11". Also illustrative of the aforesaid agents is bis(2 - hydroxy - 5 - chloro - phenyl)sulfide, a commercial variety of which, known by the designation "S-7".

Other antibacterial agents employed in the above mentioned products are, however, not adequately solubilisable in aqueus soap or anionic synthetic detergent solutions as aforesaid, but require the use of added chemicals and rather careful techniques in order to solubilize them in significant amounts, even in aqueous soap or other anionic detergent solutions.

Illustrative of such practically water-insoluble antibacterial agents are: (a) 3,4,4'-trichlorocarbanilide, commonly referred to as "TCC": and (b) a mixture of 5,4'-dibromosalicylanilide and 3,5,4' - tribromosalyicylanilide, a commercial variety of which is sold under the trademark "Diaphene".

By reason of their being practically water-insoluble and of the consequent difficulties of solubilising significant amounts thereof in soap or other anionic detergent solutions, the use of these antibacterial agents has been mostly confined to the opaque types of liquid cleansers, shampoos and the like, since they may remain suspended in their insoluble state in such products without affecting the opaque appearance of the products.

According to the present invention there is provided a detergent composition for use as a shampoo, skin cleanser and the like, consisting essentially of an aqueous solution of a soap or water-soluble anionic and/or amphoteric organic detergent, said detergent consisting of 10 to 30% by weight of the composition, and said composition containing by weight, 1 to 3% of lanolin oil, 0.3 to 1.5% of a bacteriostat consisting of one or more of the following compounds,

polyhalocarbanilides,
polyhalosalicylanilides,
polyhaloanilides of hydroxybenzoic acids,

and one or more of the following non-ionic compounds,

a polyethoxylated lanolin alcohol,
a polyethoxylated fatty acid salt of sorbitan,
a polyethoxylated alkyl phenol,

in an amount sufficient to act both as a solubilizer for the bacteriostat and to render the lanolin oil soluble in the composition.

The preferred non-ionic solubilizer compounds are,

3,4,4'-trichlorocarbanilide,
5,4'-dibromosalicylanilide,
3,5,4'-tribromosalicylanilide,

3',4'-dichloranilide of 2-hydroxy-5-chlorobenzoic acid,

An example of a mixture of such compounds, which may be used, is the mixture of 5,4'-dibromosalicylanilide and 3,5,4'-tribromosalicylanilide referred to hereinabove.

A preferred non-ionic solubilizer compound is a polyoxyethylene ether of lanolin alcohol condensed with 8 to 24 mols, preferably 16 mols, of ethylene oxide. Other examples of non-ionic solubilizer compounds are, polyethoxylated sorbitan mono-oleate and polyethoxylated nonyl phenol.

In any particular detergent composition of the invention, the amount of the lanolin oil used within the range specified should be preferably insufficient to cause substantial reduction of the anti-bacterial activity of the bacteriostat.

By means of the invention, clear and transparent liquid shampoos and the like containing said bacteriostats and lanolin oil can be made.

The compositions of the invention may be made by preparing a basic aqueous shampoo, skin cleanser, or like composition, utilizing soaps or known synthetic organic detergents of the kind above referred to, and incorporating therein said bacteriostat solubilized in the aqueous base by means of one or more of said non-ionic solubilizer compounds.

For example the bacteriostat is first dissolved in the said non-ionic solubilizer, with heating if necessary, and this mixture is then added to an aqueous dispersion of soap or water-soluble detergent of the kind above referred to, preferably with heating and stirring. The lanolin oil is preferably incorporated in the mixture of the bacteriostat and said non-ionic solubilizer.

The polyethoxylated compounds employed as solubilizer for the bacteriostat in the practice of the invention may be present in amounts, for example, of from about 2% to about 5%, preferably 4%, by weight of the composition, the higher amounts being particularly advantageous as the solubilizer serves also to solubilize the lanolin oil.

In the following table, there are shown the formulations of four typical soap or detergent basic solutions which may be utilized for the production of shampoos or skin cleansers of the invention.

TABLE 1

Composition of Detergent Solutions

	Amount in Grams			
	A	*B*	*C*	*D*
Triethanolamine lauryl sulfate (40%)	500.0	—	192.0	—
Triethanolamine dodecyl benzene sulfonate (60%)	—	333.3	—	—
Miranol C2M Concentrate	—	—	181.0	—
Concentrated Liquid Soap (36%)	—	—	—	555.5
Diethanolamide of coconut fatty acid	30.0	30.0	30.0	30.0
De-ionized water	370.0	536.7	497.0	315.5
	900.0	900.0	900.0	900.0

"Miranol C2M" is 2-cocyl-1-imidazolinium hydroxide-1-carboxymethyloxyethyl-1-carboxymethyldisodium salt.

The aqueous solutions of the detergents shown in Table I may be made up as stock solutions, for use in the preparation of compositions containing the bacteriostats.

Thus, for example, 90 gram portions of these solutions may be utilized to prepare 100 grams of the bacteriostat-containing composition.

The maximum percentage of the bacteriostat which may be solubilized in the aqueous detergent solution may conveniently be determined by trial and observation, as in the following manner:

One gram of the bacteriostat, weighed on an analytical balance to the nearest milligram, is added to 4.0 grams of the polyethoxylated non-ionic compound, weighed to the nearest one-tenth gram in a 30 milliliter beaker. The mixture is heated at 75 to 80°C., until the bacteriostat is dissolved. If occasionally a slightly higher temperature is required to hasten solution of the bacteriostat, the solution is then permitted to return to a temperature of 75-80°C. 90 grams of the detergent solution is weighed into a 150 milliliter beaker and 5.0 grams of de-ionized water is added, both these being weighed to the nearest one-tenth gram. This detergent solution is heated to 75-80°C., whereupon the solution of the bacteriostat in the non-ionic material is added at that temperature to the detergent solution with stirring. The 30 milliliter beaker in which the bacteriostat was dissolved in the non-ionic material is washed with the detergent solution to assure that all of the non-ionic material having the bacteriostat in solution therein is contained in the product. The latter is allowed to stand until it cools to around room temperature, and is then again weighed and sufficient water added to replace any water that may have been lost by evaporation so that the

total weight of the product is 100.0 grams. The product is then bottled for observation during varying periods of aging thereof.

In the case of two of the bacteriostats mentioned above, viz. TCC and Diaphene, tests were conducted to determine the amounts thereof, respectively, that could be solubilized by each of the three polyethoxylated non-ionic compounds mentioned above, viz., polyethoxylated lanolin alcohol, a polyethoxylated sorbitan mono-oleate (Tween 80) and polyethoxylated nonyl phenol (Igepal CO-630), in each of the four above-mentioned detergent solutions. In each instance, the amount of the polyethoxylated compound employed was 4% by weight of the total composition. In Table II herebelow, are set forth the data with respect to the maximum percentage of the respective bacteriostats which were solubilized in this manner. These maximum percentage figures given in Table II are the percentages of the bacteriostats solubilized in the various aqueous detergent mixtures therein shown, to the extent that the solutions remained clear during a period of aging for at least one month. It will be understood, nevertheless, that when using the non-ionic solubilizer compounds in amounts less than the above-stated 4% by weight of the composition, the resultant product may be clear when first prepared, but that precipitation of the bacteriostat may occur after a period of aging at room temperature, the aging period varying from overnight to as long as perhaps one month after preparation of the composition. In Tables II and III herein, TEA means "triethanolamine".

TABLE II

Non-ionic	Maximum Percentage of Bacteriostat Solubilized							
	TEA Lauryl Sulfate *Detergent A*		TEA Dodecyl Benzene *Detergent B*		Mixed *Detergent C*		K. Coco Soap *Detergent D*	
	Diaphene	*TCC*	*Diaphene*	*TCC*	*Diaphene*	*TCC*	*Diaphene*	*TCC*
Nimcolan S*	1.0	0.2	0.6	0.1	0.4	0.1	0.7	0.2
Tween 80	0.9	0.2	1.0	0.5	1.7	0.4	0.8	0.2
Igepal CO-630	0.9	0.3	0.7	0.2	0.9	0.3	0.8	0.2

*Trademark for a polyoxyethylene ether of lanolin alcohol with 16 mols of ethylene oxide.

In accordance with the invention the lanolin oil may be incorporated in the mixture of the polyethoxylated non-ionic solubilizer and bacteriostat, and then that mixture combined with the aqueous solution of the detergent, in the manner above described, without otherwise altering the procedure. Thus, referring to the above-described procedure, one gram of lanolin oil, replacing one gram of water may be thus utilized, to provide a composition containing 1.0% to 3% by weight of the lanolin oil. With this percentage of lanolin oil, it appeared that by the procedure described above, only the polyethoxylated lanolin alcohol served effectively to solubilize both the bacteriostat and the lanolin oil, and then only in the detergent solutions made with the single synthetic detergents (i.e. detergents A and B, *supra*) and not in the case of the soap solution or the solution of mixed synthetic detergents (i.e., detergents C and D, *supra*). In the case of detergent solutions A and B, however, it was found that with the polyethoxylated lanolin alcohol, namely, polyoxyethylene lanolin alcohol condensed with 16 mols of ethylene oxide, the presence of the lanolin oil brought about an increase in the amount of bacteriostat which could be solubilized. Thus, compared to the 1.0% of Diaphene and 0.2% of TCC solubilized in detergent A by the Nimcolan S in the absence of lanoline oil, the respective amounts thereof solubilized in the presence thereof by the Nimcolan S in detergent A were 1.2% and 0.3%. Similarly, whereas the Nimcolan S served to solubilize 0.6% of Diaphene and 0.1% of TCC in detergent B in the absence of lanolin oil, it served to solubilize 0.7% and 0.3% of the Diaphene and the TCC, respectively, in the presence of 1.0% of lanolin oil. Here again, the percentages stated for the amount of the respective bacteriostats solubilized by the Nimcolan S in the presence of the 1.0% of the lanolin oil represents concentrations which remained stable during an aging period of at least one month at room temperature.

In Table III samples designated Nos. 1 to 8, inclusive, represent aqueous compositions of the kinds referred to hereinbefore.

TABLE III

Percentage Compositions of Samples for Bacteriology Testing

Sample No.	*1*	*2*	*3*	*4*	*5*	*6*	*7*	*8*
TEA Laurył Sulfate	20	20	20	20	20	20	20	20
Schercomide SCO Extra	3	3	3	3	3	3	3	3
Nimcolan S	4	—	—	4	—	—	4	4
Tween 80	—	4	—	—	4	—	—	—
Igepal CO-630	—	—	4	—	—	4	—	—
Diaphene	1.0	0.9	0.8	—	—	—	1.2	—
TCC	—	—	—	0.2	0.2	0.3	—	0.3
Lantrol*	—	—	—	—	—	—	1.0	1.0
De-ionized Water q.s 100 in all samples								
pH of Samples	7.20	7.30	7.30	7.05	7.25	7.30	7.15	7.20

*Trademark for a liquid lanolin oil.

"Schercomide SCO Extra" is a 1;1-diethanolamide product made by reacting one mol of diethanolamine with one mol of coconut oil fatty acids and highly refined.

From the foregoing description, it will be aparent to those skilled in the art that while the invention hereof has been illustrated in embodiments wherein the water-insoluble bacteriostats are illustrated by TCC and Diaphene, the objects and advantages of the invention may be obtained with the use of other such bacteriostats, such as 2-hydroxy-5-chlorobenzoic acid 3',4'-dichloranilide, marketed under the trademark "Anobial".

As is evident from the description, and particularly the data set forth in Table II, a useful percentage of each of the bacteriostats may be solubilized in each of the four typical detergent solutions by the use of any one of the three kinds of non-ionic polyethoxylated compounds hereinbefore given. As demonstrated by the data hereinabove, each of the three specific non-ionic solubilizers has been found capable of effecting the solubilization of a greater amount of the Diaphene than of TCC in each of the detergent solutions. It is apparent that the efficiency of a given non-ionic polyethoxylated compound for solubilizing a given bacteriostat varies somewhat, depending upon the basic detergent composition utilized.

Furthermore, as already pointed out, simultaneous solubilization of lanolin oil for instance in an amount of 1.0% by weight thereof, based on the weight of the total composition, and the bacteriostat is often achieved if the non-ionic solubilizer employed is a polyoxyethlene ether of lanolin alcohol condensed with 16 mols of ethlene oxide, without causing any interference by the lanolin oil with the solubilization of the bacteriostats, the presence of the lanolin oil indeed serving to increase the amount of the bacteriostat which can be solubilized by the aforementioned polyoxyethlene ether of lanolin alcohol.

Insofar as concerns the bacteriological activity of the compositions hereof, it appears that while the bactericidal action is not sufficent to be measured by a short time killing test, such as the phenol coefficient test, the bactericidal action is nevertheless readily apparent at fairly low active ingredient concentrations in a longer term test, as shown by the data in Table VI. Bacteriostatic action against *Staphylococcus aureus*, by both of the test methods referred to above is apparent at lower concentrations of TCC than of Diaphene or of hexachlorophene, and none of these three bacteriostats shows bacteriostatic action against *E. coli* at sample dilutions of 1 : 125.

In the compositions given in the Tables hereinabove, the presence of the non-ionic polyethoxylated compounds used as solubilizers for the bacteriostat does not appear to reduce substantially the anti-bacterial activity of the bacteriostat.

WHAT WE CLAIM IS:—

1. A detergent composition for use as a shampoo, skin cleanser and the like, consisting essentially of an aqueous solution of a soap or water-soluble anionic and/or amphoteric organic detergent, said detergent consisting of 10 to 30% by weight of the composition, and said composition containing by weight, 1 to 3% of lanolin oil, 0.3 to 1.5% of a bacteriostat consisting of one or more of the following compounds,

polyhalocarbanilides,

polyhalosalicylanilides,

polyhaloanilides of hydroxybenzoic acids,

and one or more of the following non-ionic compounds,

a polyethoxylated lanolin alcohol,

a polyethoxylated fatty acid salt or sorbitan,

a polyethoxylated alkyl phenol,

in an amount sufficient to act both as a solubilizer for the bacteriostat and to render the lanolin oil soluble in the composition.

2. A detergent composition according to claim 1 wherein the bacteriostat consists of one or more of the following,

3,4,4'-trichlorocarbanilide,
5,4'-dibromosalicylanilide,
3,5,4'-tribromosalicylanilide,
3',4'-dichloranilide of 2-hydroxy-5-chlorobenzoic acid,

3. A detergent composition according to claim 1 wherein the bacteriostat is a mixture of 5,4'-dibromosalicylanilide and 3,5,4'-tribromosalicylanilide.

4. A detergent composition according to claim 1 wherein said bacteriostat is 3,4,4'-trichlorocarbanilide.

5. A detergent composition according to claim 1, 2, 3 or 4 wherein said non-ionic solubilizer compound is a polyoxyethylene ether of lanolin alcohol condensed with 8 to 24 mols of ethylene oxide.

6. A detergent composition according to claim 1, 2, 3 or 4 wherein said non-ionic solubilizer compound is a polyoxyethylene ether of lanolin alcohol condensed with 16 mols of ethylene oxide.

7. A detergent composition according to claim 1, 2, 3 or 4 wherein said non-ionic solubilizer compound is a polyethoxylated sorbitan mono-oleate.

8. A detergent composition according to claim 1, 2, 3, or 4 wherein said non-ionic solubilizer compound is a polyethoxylated nonyl phenol.

9. A detergent composition according to any of the preceding claims, wherein the amount of said non-ionic solubilizer compound is from 2 to 5% by weight of the composition.

10. A detergent composition according to any of the preceding claims wherein the amount of any lanolin oil used in the composition is insufficient to cause substantial reduction of the anti-bacterial activity of the bacteriostats.

11. The method of making a detergent composition as claimed in any of the preceding claims wherein the bacteriostat is dissolved in the said non-ionic solubilizer compound, with heating if necessary, and this mixture is then added to an aqueous dispersion of the said soap or water-soluble organic detergent, preferably with heating and stirring.

12. The method according to claim 11 wherein the lanolin oil is incorporated in the mixture of the bacteriostat and said non-ionic solubilizer compound.

13. A detergent shampoo composition made according to the method claimed in claim 11 or 12.

14. A detergent composition according to claim 1 and having ingredients as set forth in any one of the specific examples of such compositions described herein.

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